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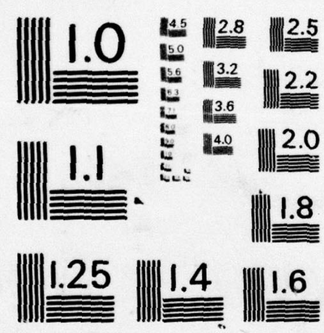

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THEORETICAL POLYMERS

Dr. T.A. KITCHENS

7 OCTOBER 1976

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This report summarizes the papers presented at the two-day UK Institute of Physics conference on theoretical methods in polymer physics. The meeting was held at the University of Leeds 5-7 July 1976 and about twenty papers were presented on the excluded volume model, various treatments of the entanglement problem, the glassy and collapse transition, and the use of the renormalization group methods

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THEORETICAL POLYMERS

"Theoretical Methods in Polymer Physics" was the subject of a two-day conference held by the Polymer Physics Group of the Institute of Physics in early July. The host was the Physics Department of the University of Leeds, which, under the Chairmanship of Professor I. Ward, is one of two or three UK physics departments heavily involved in the study of polymeric materials. About fifty people were in attendance--mostly British, but there were two or three from each of the scientifically developed nations. There were about twenty presentations, nearly half of which were invited, whose national origins had a similar distribution.

The initial invited talk, sort of an advanced reminder on entangled systems, was given by Professor P. G. de Gennes (Collège de France, Paris). He reviewed the self-consistent-field approach to polymers, pointing out its exactness in four dimensions and its equivalence to the P. Flory "phantom-chain" model. Thus, the entanglement is not even approximated. De Gennes summarized the diagrammatic perturbation method and results, which are not very good perhaps due to the large expansion parameter (on the order of N, where N is the number of elements in the polymer). However, a term-by-term comparison of the pertubation series indicates that the Heisenburg magnet and polymer problems are analogous, and this suggests the utility of the Renormalization Group. De Gennes outlined this technique and showed that, in agreement with observations, the calculations indicate that the excitation energy varies as the wave vector squared for low wave vectors. He ended with a discussion of the static scaling arguments of Edwards. These ideas lead to an exponential for the correlation length of 3/4, while 0.72 is observed.

Then followed several talks on the expansion coefficient α, the virial coefficients and related quantities. In the "phantom-chain" model, which is equivalent to a random-walk model and to the mean or self-consistent-field model, the mean-squared end-to-end distance of an N-element polymer is $\langle R_o^2\rangle = Na^2$ where a is the length of the monomer elements. The next step in the theory is to approximate reality by not allowing the polymer to overlap itself or others--the excluded-volume model. In a somewhat cruder model, suggested by C. Domb (King's College, London) some ten years ago, the monomer's ends lie on a regular lattice of points. The self-avoiding-walk (SAW) model results when the lattice points may not be doubly occupied. In the

SAW model, when the density corresponds to $\langle R_o^2 \rangle = Na^2$, the system collapses as the temperature is reduced through $T=\theta$, the Flory temperature, and the thermodynamic functions behave critically in this neighborhood.

Domb gave some new thoughts on the old problem of the expansion coefficient of a polymer chain. He first reviewed the "phantom" or random chain (where intramolecular forces are ignored) and the excluded volume (where the intramolecular forces are approximated with a pseudopotential) models. In his characteristically clear manner, he discussed the lattice model and developed the SAW model. Domb went on to scaling near critical points, the universality principle and functions that describe how the thermodynamic function scaling varies as one crosses over from one dimensionality to another--the universal cross-over functions. Using the calculations of B. McCoy (SUNY-Stony Brook) for the scaling functions of the $\langle R^2 \rangle$, $\langle S^2 \rangle$ (the mean squared radius of gyration) and other quantities for the SAW model, Domb then calculated α^2 and determined it is dependent of N^c where $c = 0.195$, in good agreement with a calculation by Flory which found $c = 1/5$.

M. A. Moore, who is moving from the University of Sussex to a professorship at the University of Manchester to work on the theory of polymers, spoke on the application of the Renormalization Group to the calculation of the virial coefficient and α^2. These quantities can be considered merely a testing ground for the use of this method to polymer problems. The test was successful, and Moore predicts extensive use of the technique.

Professor S. G. Whittington (University of Toronto) gave a very nice talk on the excluded volume effects on polymer adsorption. Much of this work is described in *J. Chem. Phys.* 63, 779 (1975) and another article to appear in December. The calculations were rather beautiful direct evaluations of the properties such as the coordination number, number of polymers of N elements attached m times to the surface, etc., for the SAW model with interfaces.

N. K. Ailewadi (Freie Universität Berlin) discussed the collapse transitions in polymers by considering the equation of state for the Lennard-Jones model of a single ring polymer. Using a statistical mechanical approach and a perturbation approach developed by Kirkwood and coworkers [see J. G. Kirkwood *et al.*, *J. Chem. Phys.* 18, 1040 (1950) and 20, 929 (1952)] for the theory of fluids, the Berlin group calculated the equation of state and the thermodynamic functions including the coefficient of expansion. The result suggests a liquid-gas type transition which is qualitative as in recent observations [see F. L. McCracken *et al.*, *Macromolecules* 6, 859 (1973)].

R. J. Fleming (Monash University, Australia) presented an extension of his previous computer Montê Carlo simulations of an excluded-volume continuum model. The earlier work was constrained to chains of less than 100 elements while the new work is limited to 500 elements. If the angle between adjacent elements is fixed to the tetrahedral angle, α^2 vs. $\sqrt{N}$ is about 50% of that calculated by Domb and coworkers on the SAW model. If the bond angle is not restricted, the α^2 is 20-30% larger than the SAW results.

The next section of the conference was on the dynamics of polymers. Sir Sam Edwards (Science Research Council) outlined his work, much the same as reported earlier by the present writer but with some additional mathematical detail (see ESN 30-1:27). Apparently Sir Sam and coworkers have not yet found a reasonable way to handle the entanglement problem, but are making progress on the cross links.

C. Bottcher (University of Manchester) spoke on kinematic phenomena in bulk polymer networks and polymer solutions. In the former case, he considered the propagation of phonons of angular frequency ω along a polymer chain based on a multiple scattering formalism. The backscattering from cross links and entanglements is especially high if the phonon wavelength, c/ω, matches the cross-link separation. The backscattering from freely rotating bonds leads to a singularity, which is dependent on the rotational energy levels, if no homogeneous broadening is introduced. The same approach applied to polymer solutions leads to a concentration dependent diffusion, suggesting that the "kinetic transition" to a phase of high viscosity is washed out at high frequencies.

M. G. Brereton (University of Leeds) reviewed the applications of the Fluctuation-Dissipation Theorems to polymer systems. He calculated the viscosity for several regimes, finding, for example, that it depends on $\sqrt{N}$ in the hydrodynamic regime. Similarily, he computed the mass flow rate for several regimes and illustrated the difficulties one has in the diffusion limit.

Brereton was followed by two contributed papers on the intrinsic viscosity of polymer solutions. P. F. Mijnlieff (Twente University of Technology, Enschede) treated the problem by considering a polymer molecule as a porous sphere with a spherically symmetric permeability. He then solved the DeBye-Brinkman equation (Navier-Stokes combined with the Darcy Equation) leading to a straightforward evaluation of the intrinsic viscosity (shear flow) and the sedimentation coefficient (translation) with no

adjustable parameters. U. M. Titulaer (RWTH, Aachen) discussed the problem of the intrinsic viscosity of solutions of stiff polymers, those with fixed bond lengths and/or angles. His work is in agreement with M. Fixman and J. Kovac [*J. Chem. Phys.* 61, 4939, 4950 (1974)] but in disagreement with O. Hassager [*J. Chem. Phys.* 60, 211, 4001 (1974)].

D. Caroline (University College of North Wales) presented one of two experimental papers at the conference, a measurement of the diffusion coefficient of polystyrenes in various solvents at 25°C near the θ-state composition. The measurements, made by photon-correlation spectroscopy, were precise to one or two percent and showed the second virial coefficient, A_2, to be zero and the intrinsic viscosity dependent on $\sqrt{M}$ for polystyrene molecular weights between 33,000 and one million. The other experimental papers, also on dynamic effects, was given by G. R. Davies (University of Leeds). He used a new experimental technique by which dielectric measurements on lossy polymers can be made down to frequencies as low as 10^{-3} Hz. This allows a detailed study of the glass transition by direct and convenient method and, in the case of poly vinylidene flouride, has shown that the locus of maximum loss in the log f vs 1/T plane curves very strongly near T_g, indicative of a very rapid slowing down of molecular motions. A simple two-site model with correlative motion, in the context of the mean field approximation, yields a good fit for the locus of maximum loss but cannot account for all the features of the data.

Professor M. Gordon (University of Essex) gave a very intriguing talk on the application of graph theory to the glass transition. He developed the theory of the glass transition and contrasted it with the θ, or condensation transition. After a very elegant presentation of the use of graph theory to enumerate the possible configurations of a polymer utilizing such lattice coverages as the "Manhatten Traffic Regulation" (where square-lattice lines are covered going alternately east and west, or north and south--all are "one-way") which involve "Hamilton walks" (all lattice vertices are covered once and only once) or Euler walks (each lattice line traversed once and only once), Gordon raised the ultimate question--which has begun to receive attention since it appears that the glasses disobey the third law--are the glasses even thermodynamic? If the answer is no, then the graph theory may not be of much help in understanding the glassy transitions.

Gordon's talk was followed by one given by P. Irvine, also from Essex. Irvine discussed the use of a truncation theorem

which allows the phase changes and the critical points to be found rather easily from the free energy of mixing of the polymer solutions. The method is especially useful to compare with the phase-diagrammatic data from the pulsed-induced critical scattering. Computer programs have been prepared at Leeds for this purpose.

In the final talk on the dynamic properties of polymers, G. J. Morgan (University of Leeds) spoke on the thermal conductivity, K, of polymer systems. He first pointed out that the theories of K for solids and liquids are on an entirely different basis. For liquids, the Fokker-Planck equations play the central role, and this approach is completely inadequate at high frequencies where the conduction is more like the solid. For polymer solutions, or for that matter any amorphous material, there is no adequate theory. Because of the high coordination number in the polymer case, Morgan argued that solid-like wave packets of plane waves, i.e., phonons, should be appropriate. Indeed, the predictions of this approach provide that $K \alpha T^2$ for $T < 1°K$ and that K is proportional to the specific heat at higher T in fair agreement with observations. However, the effects of the glass transition do not show in the K data. He then discussed the scattering mechanisms, of which quantum mechanical tunneling effects, which strongly contribute to the behavior below 1°K, and short-range-order Rayleigh scattering are the most important. Morgan pointed out that K along drawn polymers is enhanced by a factor of about 20. Here the theory has developed along the lines of a resistive network composed of low resistances in a chain along nodes with higher resistance cross links, randomly distributed on the nodes.

The final two papers of the meeting were on the structural properties of polymers. The first of these contributed papers was given by R. Lovell (Cambridge), who described a new method of numerically sharpening wide-angle x-ray diffraction patterns from aligned glassy polymers. The structural model on which the technique is based assumes that a uniaxially aligned glassy polymer contains entities with fiber symmetry, the major axes of which are distributed about the alignment direction of the specimen. The method can then remove the effects of the distribution of orientations of these fiber entities. The pattern resulting from the iterative sharpening procedure contains the information on the molecular conformation and packing but also the effects from the disorder in the diffracting domains. The second paper involved the computer simulation of twinning in a polyethylene crystal. This work was reported by N. A. Geary (Liverpool). The (110) and (310) twinning modes have the smallest magnitude of sheer and were predicted to be equally likely, but

experiments showed the (110) mode to be predominant [see M. Bevis and P. S. Allan, *Chem. Soc. (London)* 3, 93 (1974)]. The preliminary results of the simulation suggest that the (110) mode has much lower energies in agreement with the observations.